

# AGGREGATION OF PETROLEUM ASPHALTENS IN THREE DIFFERENT CRUDE OILS

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## Introduction

Asphaltenes, the most polar and heaviest compounds of oil, associate themselves in solution to form complex colloidal structures. Asphaltenes causes serious problems in oil recovery, oil-carrying pipelines, and refinery operations, and many of them being related to the presence of aggregates in the heavy fraction. These difficulties have motivated an important research effort aimed at understanding the colloidal properties of asphaltenes. Despite this research effort (reviewed, e.g. in ref 1), there is currently no clear picture of the structure of asphaltene.

It is generally believed (but by no means proven) that asphaltenes retain such a structure in solution, the aliphatic/naphthenic cluster being solvate to some amount. This structure might be responsible for the micellar-like properties observed in asphaltene solutions. These entities associate in turn into structures of larger scales (aggregates) whose properties remain to a large extent unknown and is the subject of a number of hypotheses and speculations.<sup>2</sup> These aggregates have sizes and molecular weights that depend strongly on the thermodynamic conditions (e.g., temperature, pressure, solvent nature, and/or composition). A number of these studies have been performed using SANS at IPNS.<sup>3,4</sup>

We have isolated asphaltenes from three different crude oils: Maya (a Mexican super heavy crude), Khafji (an Arabian heavy crude), and Iranian Light (an Iranian intermediate crude). These are a unique set samples because they are from different crude oil taken under identical conditions. Such a set of samples is not in the literature. Based on our experience in SANS of asphaltenes from Maya crude oil,<sup>4</sup> we expect that the comparison of these three asphaltenes will help define their role in difficulties in processing.

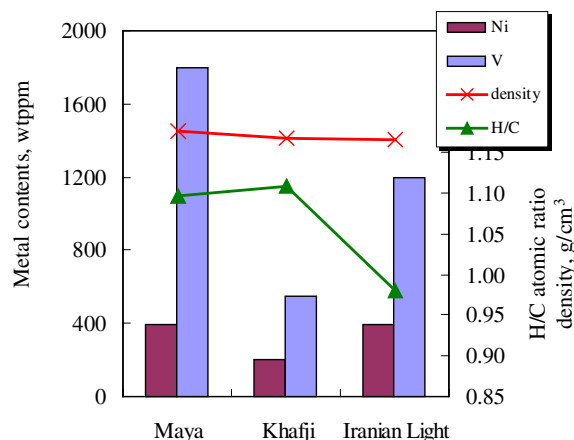
The purpose of this experiment is to determine whether the structural units of these aggregates are micellar or molecular in nature and with the purpose of shedding some light on the structure of asphaltene aggregates from different oils and their evolution with solvent and temperature condition.

## Experimental

**Sample Preparation.** The residua (> 500 .) was obtained by vacuum distillation of three crude oils. Asphaltenes were isolated by addition of a 20:1 excess of *n*-heptane to each of the residua at 25 . The suspension was stirred 1 h at 100 . in the autoclave. After cooling down and leaving at 25 . overnight, the suspension was filtered. The precipitate was washed with *n*-heptane twice and dried. The yields of asphaltenes (precipitates) of Maya, Khafji, and Iranian Light are 24.9, 14.2, and 6.3wt%, respectively. **Table 1** and **Figure 1** show elemental analysis data of the asphaltenes.

**Table 1. Elemental analysis data of asphaltenes.**

	Maya	Khafji	Iranian Light
elemental, wt %			
carbon	82.0	82.2	83.2
hydrogen	7.5	7.6	6.8
sulfur	7.1	7.6	5.9
nitrogen	1.3	0.9	1.4
oxygen	1.2	1.1	1.5
H/C	1.10	1.11	0.98
metals, wtppm			
Ni	390	200	390
V	1800	550	1200
density, g/cm <sup>3</sup>	1.1767	1.1683	1.1669



**Figure 1. Metal contents, H/C ratio, and density of asphaltenes**

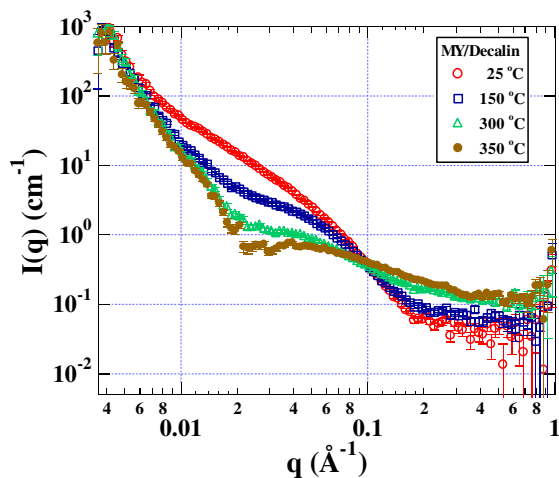
Asphaltene of Maya (As-MY) is the heaviest and contains the most amount of metals among the three asphaltenes. As-KF is medium heavy and contains the least amount of metals. H/C atomic ratio of As-KF is the highest, and this could be interpreted as the lowest aromaticity. As-IL is the lightest, but contains much nitrogen and metals. It has the lowest H/C atomic ratio, meaning the highest aromaticity. These properties are considered to affect aggregation phenomena of asphaltene molecules much.

**Small Angle Neutron Scattering.** An aliquot of the 5 wt% asphaltene solution in 1-methylnaphthalene-*d*<sub>10</sub>, quinoline-*d*<sub>7</sub>, or decalin-*d*<sub>18</sub> was loaded in a stainless steel cell constructed especially for SANS measurements. The wall thickness of 1 mm and a sample thickness of 3 mm make the total path length of 5 mm for neutrons. Small angle neutron scattering was performed by placing the sample cell in a boron nitride furnace tube in the small angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The temperature of the furnace was measured using type K thermocouple and maintained within 0.5 . using a Micricon controller. At each temperature, the sample was equilibrated for about 30 min prior to SANS measurements. The temperature was increased at the rate of 5 ./min. The SAND instrument uses neutrons produced in pulses by spallation due to the deposition of 450 MeV protons on a depleted uranium target, followed by a solid methane moderator (24 K) yielding a wave length range of 1-14 . Detection of scattered neutrons was accomplished with a 40 x 40 cm<sup>2</sup>, 2.5 cm thickness area detector, and the wave length of the scattered neutrons was determined by their times of flight. Data were corrected for unit transmission of the sample, the

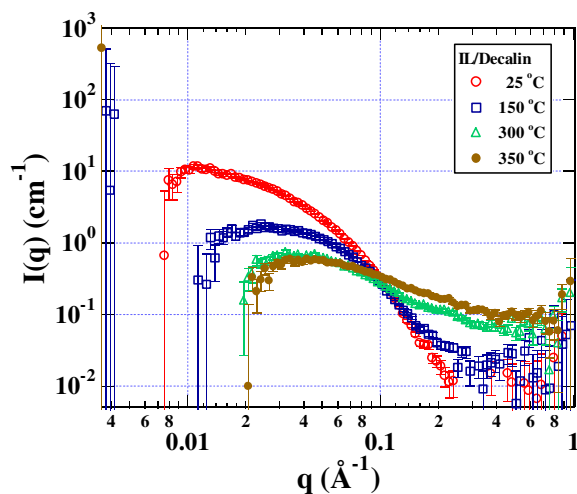
scattering from the stainless steel cell, and incoherent scattering. The accessible  $q$  range ( $q = 4\pi\sin(\theta)/\lambda$ , where  $\theta$  is the wavelength of the probing neutrons and  $\lambda$  is half the scattering angle) using SAND is from 0.0035 to 0.6  $\text{\AA}^{-1}$ .

## Results and Discussion

The scattering intensity as a function of scattering vector for As-MY and As-IL in decalin- $d_{18}$  are shown in **Figure 2** and **3**. All of samples were measured at 25, 150, 300, and 350  $^{\circ}\text{C}$ .



**Figure 2.** SANS data of As-MY in decalin- $d_{18}$  at 25-350  $^{\circ}\text{C}$ .



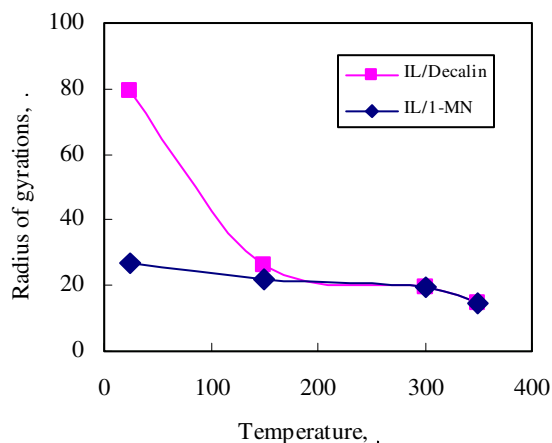
**Figure 3.** SANS data of As-IL in decalin- $d_{18}$  at 25-350  $^{\circ}\text{C}$ .

Power law slope at low  $q$  region (under 0.02  $\text{\AA}^{-1}$ ) in **Figure 2** shows fractal network. Fractal network is formed only with As-MY in decalin- $d_{18}$  system, and it remained even at 350  $^{\circ}\text{C}$ . Coking reaction seems to start in this system before aggregates are completely dispersed.

Incoherent scattering intensities of higher  $q$  region (over 0.1  $\text{\AA}^{-1}$ ) of As-MY and As-IL at 25 and 150  $^{\circ}\text{C}$  are suppressed than at higher temperatures. Incoherent scattering intensities depend not on the aggregate structure but only on the elemental composition in the neutron beam path. Therefore, the suppression means that carbon

and hydrogen contents in the beam path are fewer at low temperature. This indicates As-MY and As-IL are making precipitation in decalin- $d_{18}$  solutions at lower temperature than 150  $^{\circ}\text{C}$ . Precipitation is more with As-IL than with MY, and very few with KF. It may reflect the higher aromaticity of As-IL.

Radius of gyrations of As-IL aggregates are shown in **Figure 4**. The values are estimated with Guinier analysis assuming the compact particles. At lower temperature than 200  $^{\circ}\text{C}$ , especially at 25  $^{\circ}\text{C}$ , size of As-IL aggregates in decalin- $d_{18}$  are much larger than in 1-methylnaphthalene- $d_{10}$ .



**Figure 4.** Radius of gyrations of As-IL aggregates in decalin- $d_{18}$  and 1-methylnaphthalene- $d_{10}$ , at 25-350  $^{\circ}\text{C}$ .

Ellipsoidal fitting of polydisperse system is more suitable to the scattering intensity of As-IL in decalin- $d_{18}$  at 25  $^{\circ}\text{C}$  than compact particle Guinier fitting. The length of the ellipsoid is 170  $\text{\AA}$ . On the other hand, scattering intensity of As-IL in 1-methylnaphthalene- $d_{10}$ , is well fitted with the spherical particle with the radius of gyration of 27  $\text{\AA}$ . Both aggregates got smaller with increasing temperature, and became compact particle of radius of gyration of 15  $\text{\AA}$  at 350  $^{\circ}\text{C}$ .

The  $I(q)$  data turn over in the low  $q$  region (around 0.02  $\text{\AA}^{-1}$ ) at higher temperatures (**Figure 3**). This is clearly due to interparticle interactions. To analyze these quantitatively, we must know the exact nature of the interparticle interactions and the chemical or physical natures of the aggregates. These are challengeable tasks in the future.

## Acknowledgment

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## References

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